Basic Performance of the Agilent 7700s ICP-MS for the Analysis of Semiconductor Samples

Application Note

Semiconductor

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Abstract

Agilent ICP-MS systems have become the benchmark for accurate low-level analysis of trace contaminants across a wide range of high-purity chemicals used in the semi-conductor industry. As the first commercial ICP-MS to offer reliable and routine cool plasma operation, the Agilent 4500 Series ICP-MS set the standard for low level analysis of the previously problematic elements Na, K, Ca and Fe. Building on the success of the 4500 Series, the Agilent 7500s ICP-MS provided additional sensitivity, stability and matrix tolerance, while the Agilent 7500cs ICP-MS introduced new levels of performance through the provision of an Octopole Reaction System (ORS) operating in both collision and reaction modes.

The newly-developed Agilent 7700s ICP-MS further extends the performance of the technique for routine semiconductor applications by combining unmatched sensitivity, matrix tolerance, interference removal and stability in a single reliable and easy to use system.

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Introduction

The Agilent 7700 Series ICP-MS product line includes the 7700s model, which is configured specifically for semiconductor applications, with a PFA nebulizer, Pt interface and high-transmission ion lens. Development of the 7700 Series was focused on ensuring "ease of use", while improving on the sensitivity and interference-removal capability of the 7500cs. To meet these goals, many new features have been introduced in the 7700s, including much smaller size, easier maintenance, and lower cleanroom service requirements (20% lower exhaust flow and 3.5x lower pressure drop than the 7500cs). The 7700s also introduces a new, robust, frequency matching RF generator for improved performance in volatile organic solvents, and a 3rd generation ORS[3] collision reaction cell.

Basic Performance of the 7700s

The 7700s incorporates a new interface, ion lens and the newly-developed ORS[3], to deliver better ion transmission and lower backgrounds than the 7500cs. In general, the sensitivity (cps/ppt) of the 7700s is approximately 40% higher than that of 7500cs, and the new off-axis lens configuration reduces random background noise by half. The result is that the 7700s has much lower Detection Limits (DLs) and Background Equivalent Concentrations (BECs) than its predecessor. Table 1 shows the normal plasma DLs and BECs obtained on the 7700s in a matrix of 1% HNO_3. Elements with a * may also be measured in cool plasma (BEC and DL in brackets). Figure 1 shows the preferred-mode DL of the 7700s compared to the 7500cs. In all cases, the 7700s DL was lower, notably for elements with plasma-based interferences (for example ^{56}Fe, ^{78}Se).

Improved Interference Removal

The newly developed ORS[3] has longer rods and a smaller internal diameter, and operates at higher frequency and higher cell gas pressure than the cell fitted to the 7500cs. As a result, higher bias voltages may be used, which improves the removal of polyatomic interferences in helium (He) mode with Kinetic Energy Discrimination (KED), and also promotes Collision Induced Dissociation (CID) for relatively weakly-bound polyatomic ions such as ArO^+ (dissociation energy 0.6 eV) and $ArAr^+$ (dissociation energy 1.3 eV). More effective removal of these background (plasma-based) polyatomic ions provides much lower DL and BEC for many elements, although reaction mode (H_2 cell gas) provides the lowest DL and BEC for several elements including Fe and Se in the highest purity semiconductor samples.

Table 1. 7700s ICP-MS BECs and DLs in 1% HNO_3

Mass	Element	BEC ppt	DL ppt	Mode
7	Li*	0.2 (0.01)	0.06 (0.01)	No gas
9	Be	0.04	0.05	No gas
11	B	6	1	No gas
23	Na*	200 (0.5)	4 (0.3)	No gas
24	Mg	0.2	0.07	No gas
27	Al*	20 (0.2)	0.6 (0.3)	No gas
39	K*	250 (0.5)	10 (0.3)	H_2
40	Ca*	5 (2)	2 (1)	H_2
48	Ti	0.2	0.2	He
51	V	0.1	0.1	He
52	Cr*	10 (0.03)	0.7 (0.09)	He
55	Mn*	0.6 (0.05)	0.6 (0.1)	He
56	Fe*	7 (0.5)	0.6 (0.2)	H_2
59	Co*	0.08 (0.01)	0.09 (0.06)	He
60	Ni*	1 (0.03)	0.6 (0.1)	He
63	Cu*	6 (0.6)	0.8 (0.4)	He
64	Zn	0.6	0.5	He
71	Ga*	0.07 (0.01)	0.05 (0.01)	He
74	Ge	0.01	0.05	He
75	As	0.07	0.4	He
78	Se	0.5	0.9	H_2
85	Rb*	0.2 (0.01)	0.2 (0.03)	He
88	Sr	0.01	0.04	He
90	Zr	0.06	0.05	He
93	Nb	0.01	0.02	He
98	Mo	0.04	0.07	He
107	Ag	0.04	0.03	He
114	Cd	0.02	0.06	He
118	Sn	0.5	0.2	He
121	Sb	0.03	0.04	He
138	Ba	0.01	0.02	He
178	Hf	0.01	0.01	He
181	Ta	0.01	0.01	He
182	W	0.01	0.03	He
197	Au	0.05	0.05	He
205	Tl	0.01	0.03	He
208	Pb	0.1	0.09	He
209	Bi	0.02	0.04	He
232	Th	0.01	0.01	He
238	U	0.01	0.01	He

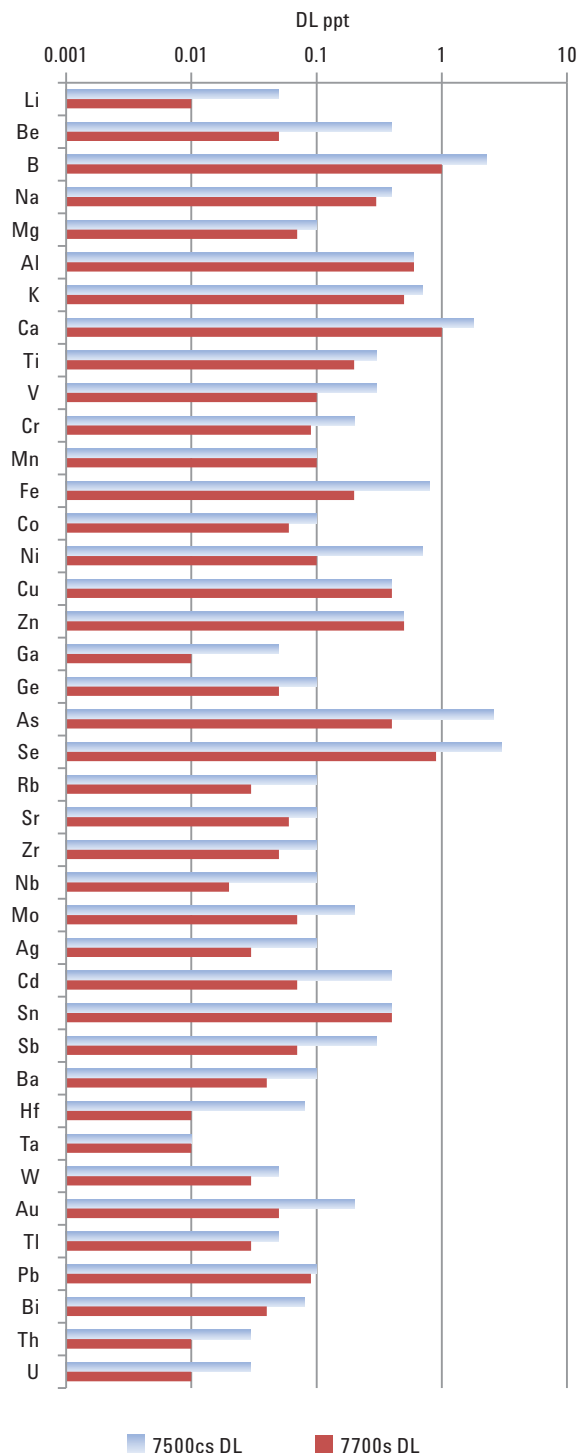*Elements may also be measured in cool plasma (BEC and DL in brackets).

DL ppt

Li
Be
B
Na
Mg
Al
K
Ca
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Rb
Sr
Zr
Nb
Mo
Ag
Cd
Sn
Sb
Ba
Hf
Ta
W
Au
Tl
Pb
Bi
Th
U

7500cs DL   7700s DL

Figure 1.   DL comparison for Agilent 7700s and 7500cs ICP-MS.

The enhanced He mode operation of the ORS[3] on the 7700s delivers dramatically improved detection of phosphorus, with DLs and BECs improved by a factor of 10 to 50 compared with conventional collision/reaction cell ICP-MS. The 7700s He mode calibration curve for phosphorus in 1% HNO_3 is shown in Figure 2.
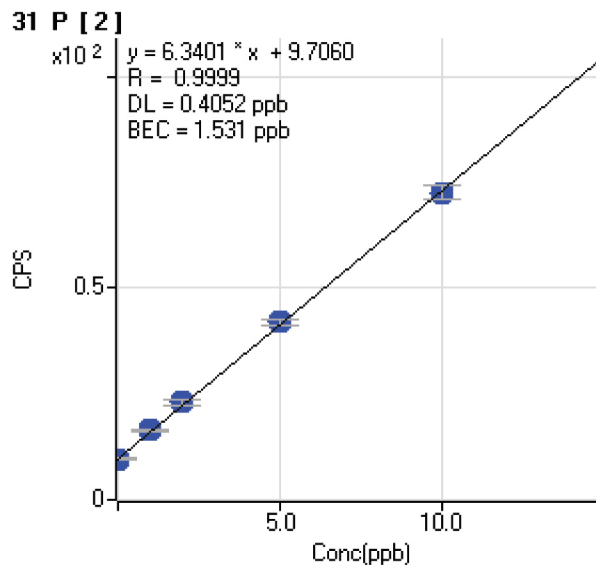

31 P [2]

$y = 6.3401 * x + 9.7060$
R = 0.9999
DL = 0.4052 ppb
BEC = 1.531 ppb

CPS

Conc(ppb)

Figure 2.   7700s ICP-MS He mode calibration for ^{31}P in 1% HNO_3.

The new ORS[3] also delivers better performance in reaction mode with H_2 cell gas, due to the higher cell gas density and the higher energy of the collisions between the interfering ions and the cell gas. This gives lower DLs for elements such as Si (measured directly at mass 28), and reduces the need for highly reactive cell gases such as NH_3, which has a strong tendency to form multiple cluster ions in the cell and is therefore not generally suitable for variable or complex process chemical matrices, or for multi-element analysis. The performance of the 7700s in H_2 reaction mode is illustrated in Figure 3, which shows the calibration curve, DL and BEC for ^{28}Si in a matrix of 1% HNO_3. It should be noted that the pure water used in the examples in Figures 2 and 3 was normal Milli-Q water and not further purified. Silicon is expected to be present at high concentration in such water and blank contamination would therefore have contributed to the BEC.
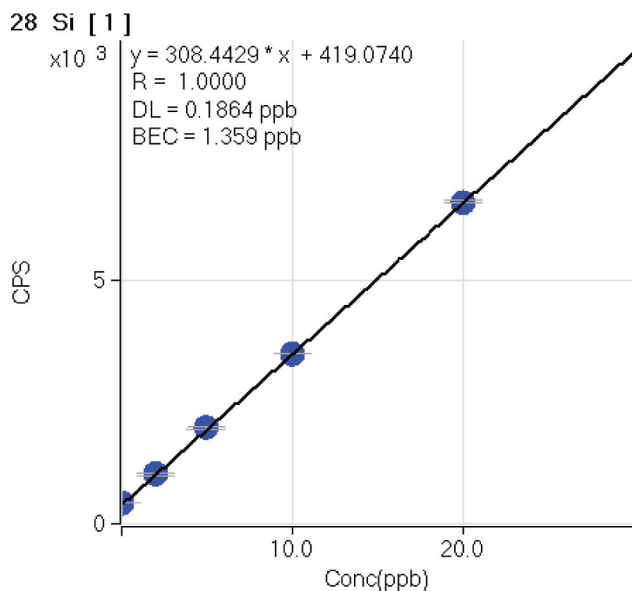
28 Si [1]

$y = 308.4429 * x + 419.0740$
$R = 1.0000$
$DL = 0.1864$ ppb
$BEC = 1.359$ ppb

Figure 3.   7700s ICP-MS H_2 mode calibration for ^{28}Si in 1% HNO_3.

Long Term Stability

Long term (9 hours) stability was measured for several elements spiked at 100 ppt in 1% HNO_3. Sampling and data acquisition was done every 35 minutes. Raw count rate signal drift was within ± 5% over the 9 hour sequence, and the %RSD was < 3% for all analytes. The excellent long term stability of the 7700s operating in He mode is shown in Figure 4.
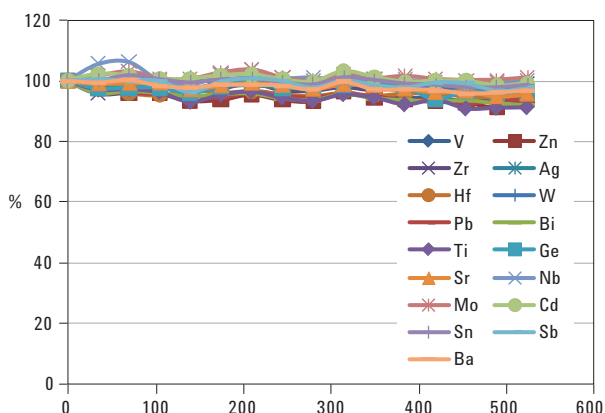
Figure 4.   Nine hours stability of 7700s ICP-MS operating in He mode
            (100 ppt spike in 1% HNO_3).

Other Reaction Gases

The 7700s has both collision (He) and reaction (H_2) cell gas lines fitted as standard, but can also have an optional 3rd cell gas line fitted for specialized applications. In the semiconductor industry, this includes analyses where optimum interference removal requires a highly reactive cell gas such as NH_3. While the requirements for such highly reactive cell gases are very small, there are some specific cases where such gases offer the lowest DLs.

One example of the use of highly reactive cell gases is illustrated in Figure 5, which shows the calibration for V in concentrated HCl, using NH_3 mode. The intense ClO interference which affects the only useful isotope of V at mass 51 is not very reactive with H_2, so H_2 cell mode does not give sufficiently good interference removal for the lowest DL to be achieved in the highest purity HCl, such as (TAMAPURE-AA100 (20%)). As can be seen in Figure 5, the 7700s ICP-MS operating in NH_3 mode gives effective removal of the ClO interference in undiluted (20%) HCl, providing a BEC and DL of only 2.3 ppt for V.
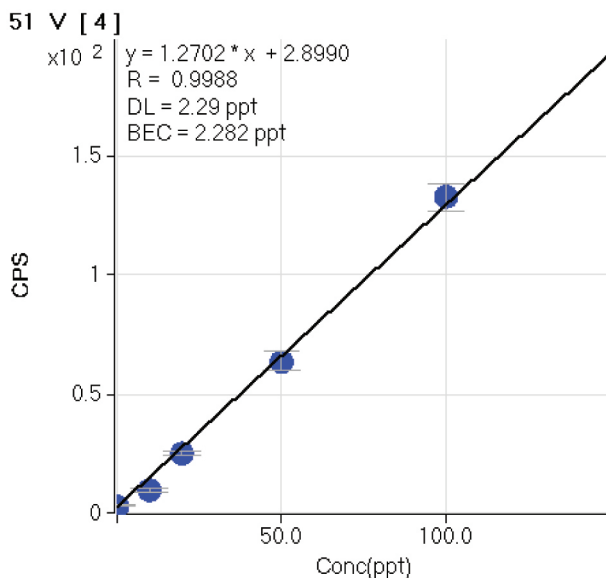
51 V [4]

$y = 1.2702 * x + 2.8990$
$R = 0.9988$
$DL = 2.29$ ppt
$BEC = 2.282$ ppt

Figure 5.   Vanadium calibration in undiluted HCl, using NH_3 mode.

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Improved Analysis of Organic Solvents

The 7700s incorporates a newly developed frequency matching RF generator, which responds more quickly to any change of impedance in the plasma, compared to a conventional fixed frequency matching system. A wide range of organic solvents can therefore be introduced without causing disturbance of the plasma.

The most important organic solvent in the semiconductor industry is isopropyl alcohol (IPA). IPA is frequently used to clean silicon wafers and must be analyzed periodically to check for contamination by trace metallic elements. For most organic solvents (inducing IPA), an organics torch with a 1.5 mm internal diameter (id) injector is used, but a torch with a 1.0 mm id injector is also available for the most volatile solvents.

Figure 6 illustrates the single-ppt and sub-ppt DLs and BECs achieved on the 7700s ICP-MS for the analysis of undiluted IPA. The elements Ti, V, Co, Zn, As, Sr, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, Sn, Ba, W, Ir, Au, Tl, Bi, Th and U were measured in normal hot plasma conditions (in He, H_2 or no gas mode) and the remaining elements were measured in cool plasma.

Figure 7 shows the excellent raw count rate stability for a 100 ppt spike of several elements in undiluted IPA, measured continuously over 4 hours. Total signal variation was < 5 %RSD.
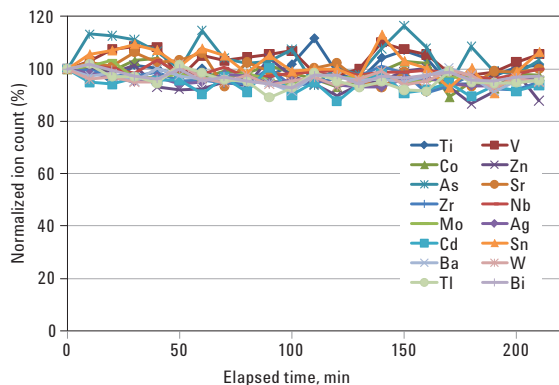

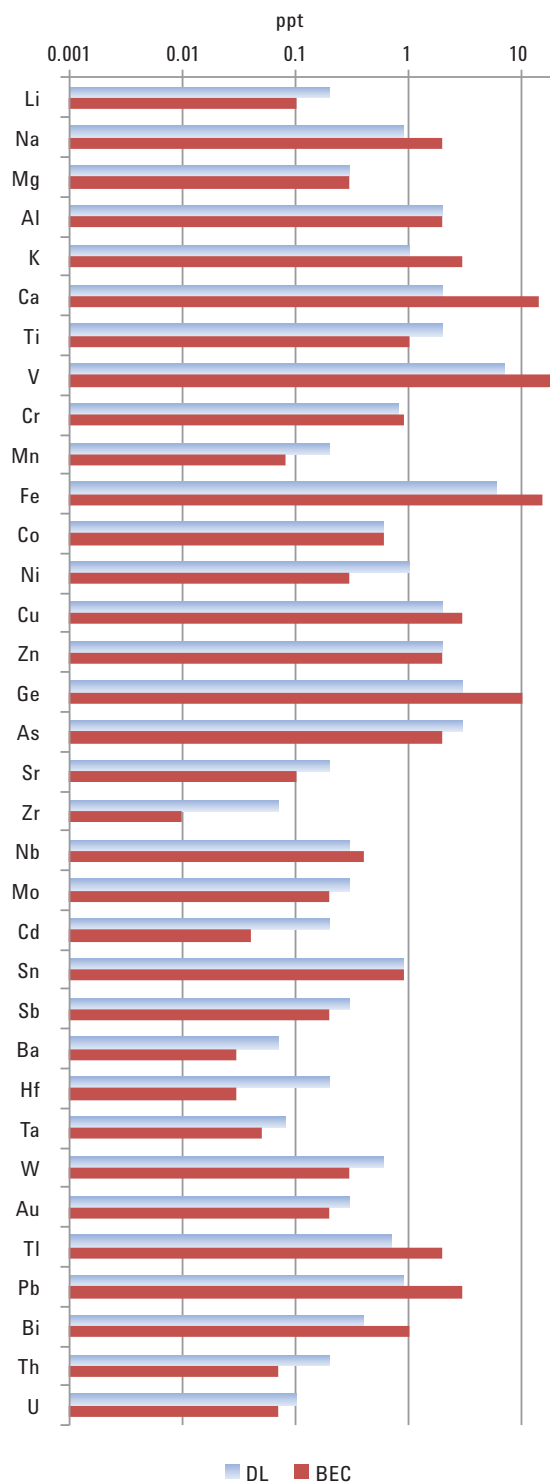*Figure 7.   Four hours stability of He mode (100 ppt spiked into IPA).*

Figure 6.   7700s ICP-MS DLs and BECs in undiluted IPA.

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Cool Plasma Operation

As the manufacturer responsible for the development of the first ICP-MS capable of routine operation under cool plasma conditions (4500 Series), Agilent was largely responsible for the initial acceptance and widespread use of ICP-MS in the semiconductor industry. In each subsequent generation of Agilent ICP-MS instrument, cool plasma has been further refined, allowing analysts to make use of the widest range of analytical techniques for interference removal. The 7700s provides a further enhanced cool plasma mode of operation, with improved robustness and stability due to the use of the new frequency matching RF generator.

The exceptional cool plasma performance of the 7700s is demonstrated in Figure 8 which shows the long term stability of several elements in 1% HNO_3.
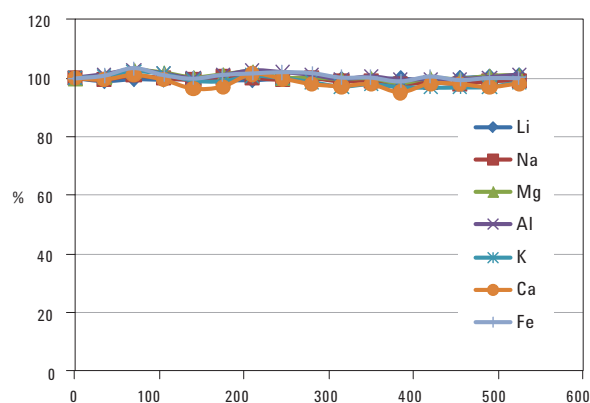
Figure 9.   Four hours stability of cool plasma mode (100 ppt spiked into IPA).

Figure 8.   Nine hours stability of cool plasma mode (100 ppt spike in 1% HNO_3).

Cool plasma on the 7700s is also suitable for the measurement of organic solvents. Due to the high volatility of IPA (boiling point 82.4 °C), it may be difficult to keep the ICP stable, particularly when switching between cool and hot plasma modes within an analysis. This issue is resolved with the new frequency matching generator of the 7700s, as demonstrated in the data shown in Figure 9. The elements in Figure 9 were measured in cool plasma, while the corresponding data shown in Figure 7 were measured in normal hot plasma conditions. The plasma conditions were switched automatically between cool plasma and hot plasma for each sample in the analytical sequence, illustrating the robustness and matrix tolerance of the new 7700s RF generator.
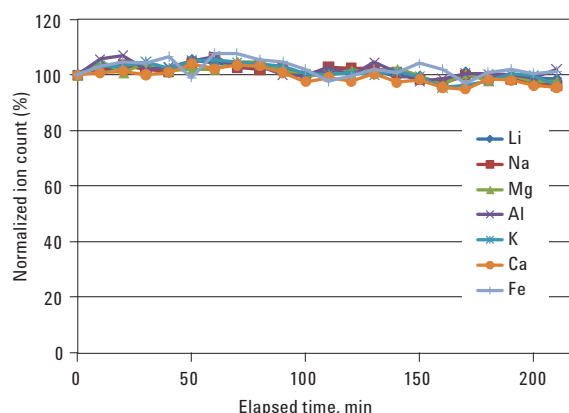
Conclusions

In addition to greatly reduced cleanroom setup and operating costs due to its small size and low service requirements, the Agilent 7700s ICP-MS provides lower DLs and BECs, and higher sensitivity than the Agilent 7500cs ICP-MS.

Moreover, the newly developed, 3rd generation ORS[3] can be fitted with up to 3 cell gas lines (2 are included as standard), allowing total flexibility. The new ORS[3] cell improves performance for several critical elements by increasing the efficiency of both collision and reaction mode, and providing enhanced CID. These developments now allow several elements like phosphorus to be determined at lower concentrations than previously possible.

The robust RF generator of the 7700s also improves the analysis of volatile organic solvents, simplifying the analysis of a variety of process chemicals. Improved matrix tolerance and stability is provided, both for conventional analysis and cool plasma operation.

Details regarding the operating conditions and performance achieved in the analysis of specific semiconductor chemicals are provided in the tuning guide that ships with every Agilent 7700s ICP-MS instrument.

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